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- (71) Applicant (for all designated States except US): **JOHNSON MATTHEY PUBLIC LIMITED COMPANY** [GB/GB]; 2-4 Cockspur Street, Trafalgar Street, London SW1Y 5BQ (GB).
- (72) Inventor; and  
(75) Inventor/Applicant (for US only): **TWIGG, Martyn, Vincent** [GB/GB]; 108 Ermine Street, Caxton, Cambridge CB3 8PQ (GB).
- (74) Agent: **WISHART, Ian, Carmichael**; Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH (GB).
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**WO 01/19500 A1**

(54) Title: **REGENERATING SULPHUR POISONED DIESEL CATALYSTS**

(57) Abstract: A diesel (compression ignition) engine having combustion management means and an exhaust gas aftertreatment system without an NO<sub>x</sub> trap, which system comprising a platinum group metal (PGM) catalyst liable to be poisoned by fuel sulphur to cause significant degradation of catalyst performance, which engine is fuelled, at least intermittently, by a diesel fuel containing such levels of sulphur as to cause poisoning of the catalyst, wherein the combustion management means is effective to modulate the air/fuel ratio ( $\lambda$ ) to 0.90, preferably 0.95, or richer for a time which is in aggregate sufficient to cause release of significant quantities of sulphur-containing species from the catalyst or catalyst components, whereby the catalyst is regenerated.

5        **REGENERATING SULPHUR POISONED DIESEL CATALYSTS**

      This invention concerns improving catalyst performance, especially where the catalyst is a catalyst in the exhaust gas from a combustion system such as a lean combustion internal combustion engine, where the fuel for the engine is a "higher sulphur" fuel.

      It is well known that fuels, including gasoline or diesel (gas-oil) fuels containing relatively high sulphur content, e.g. about 350 ppm in the case of diesel fuel, lead to a number of disadvantages when trying to clean-up the exhaust gases by some form of catalytic aftertreatment. During the combustion process, sulphur in the fuel is converted to sulphur dioxide (SO<sub>2</sub>) which poisons in particular platinum catalysts. The platinum catalyst itself catalyses the oxidation of SO<sub>2</sub> to SO<sub>3</sub> which adsorbs strongly onto the surfaces of platinum particles and is extremely effective as a catalyst poison. Further contributions to poisoning problems arise from the formation of base metal sulphates from the other components of a catalyst formulation, which sulphates can act as a reservoir for poisoning sulphur species within the catalyst.

      A number of catalysts may be used in association with such lean combustion engines as diesel engines, including oxidation catalysts, NO<sub>x</sub> storage catalysts and the combination of platinum oxidation catalyst and a particle filter/trap which utilises the formation of NO<sub>2</sub> from NO in the exhaust gases, and the combustion of trapped sooty particles by reaction with the NO<sub>2</sub>. This system is described in, for example, our EP 341,832 and such systems are commercially available as the "CRT"<sup>TM</sup> continuously regenerating technology. In all these cases, the unavailability of low (<50ppm) sulphur fuel, even for one or two tankfuls, can seriously degrade the performance of the catalyst, and performance may never recover fully, or some other damage may be caused to the engine system or catalyst system.

      There is therefore a real need for a system or a method of operation that will permit either the occasional tank filling with high sulphur fuel or even more continuous operation using high sulphur fuel, without causing undue damage to the catalyst or the complete system.

We have previously proposed, in WO99/11910, a system for the reduction of sulphur poisoning in an underfloor catalyst, by the initiation of an engine operating system, e.g. by enriching the exhaust gases with CO and/or hydrocarbon, to raise the temperature of the catalyst to at least 550°C. Such a system has particular application to a gasoline-  
5 fuelled engine operating as a stoichiometric ( $\lambda=1$ ) engine.

We have now developed an alternative system which may be more flexible under at least some conditions, and is not limited to the achievement of such high temperatures. Accordingly, the present invention provides a diesel (compression ignition) engine having  
10 combustion management means and an exhaust gas aftertreatment system without a NO<sub>x</sub> trap, which system comprising a platinum group metal (PGM) catalyst liable to be poisoned by fuel sulphur to cause significant degradation of catalyst performance, which engine is fuelled, at least intermittently, by a diesel fuel containing such levels of sulphur as to cause poisoning of the catalyst, wherein the combustion management means is  
15 effective to modulate the air/fuel ratio ( $\lambda$ ) to 0.90, preferably 0.95, or richer for a time which is in aggregate sufficient to cause release of significant quantities of sulphur-containing species from the catalyst or catalyst components, whereby the catalyst is regenerated.

The combustion management means may initiate the necessary level of enrichment according to a pre-determined frequency, or in response to a condition indicating catalyst poisoning or the danger of catalyst poisoning, for example by some form of sensing of sulphur levels either directly or indirectly. This may be achieved, for example by on-board diagnostics indicating that the catalyst is no longer performing in the correct and  
25 appropriate manner.

The combustion management means ideally forms part of a conventional electronic engine control unit.

30 Conventional Diesel engines normally operate under lean conditions, with a considerable excess of oxygen over that required for combustion of the hydrocarbon fuel. However, some engines may operate at a slightly rich condition in some parts of their

load/speed map. Such regions can be extended by appropriate control of fuelling, EGR rates, and if necessary throttling air intake to one or more of the cylinders.

Modern diesel engine designs are tending towards so-called "common-rail" fuel injection systems. The use of these are particularly preferred in the present invention because of the ability to control quantity and timing of fuel injection. Accordingly, one method of operating the present invention is to incorporate, during the enriched operating conditions, such a quantity of fuel post combustion in the main power stroke, as to reach in the exhaust gases,  $\lambda$  of 0.95 or richer. This may be achieved by generally known means.

10 The post combustion enrichment may be in one or more of the cylinders, providing that the overall air fuel ratio reaches 0.95 or richer. Of course, the quantity of air may be restricted as an alternative, or in addition, providing that driveability is not noticeably affected.

It is envisaged that the simplest method of operating is to cause enrichment to a pre-determined level for the necessary time. However, it may be more advantageous to ramp up to either a peak or a plateau, or to carry out a series of peak enrichments. The ideal format may be determined for any particular engine and catalyst system by routine testing. The enrichment profile may be varied according to operating conditions.

20 We believe, although we do not wish to be restricted by theory, that the present invention permits the release of sulphur both as  $\text{SO}_2$  and as  $\text{SO}_3$  from a poisoned catalyst surface. It is preferred to avoid catalyst components which store or retain sulphur species.

The air/fuel ratio necessary for successful regeneration depends on the temperature, and the catalyst concerned. For practically convenient temperatures to be effective normally  $\lambda = 1$ , or a slightly richer environment is required, suitably to  $\lambda = 1.1$ . Regeneration times are lower with more strongly reducing conditions. Typically  $\lambda = 0.95$  is appropriate at temperatures in the range  $250^\circ\text{-}500^\circ\text{C}$ . More strongly reducing conditions can result in formation of increasing amounts of undesirable hydrogen sulphide ( $\text{H}_2\text{S}$ ).

30 This has a disagreeable odour, and is itself a powerful catalyst poison that strongly adsorbs to metal catalyst surfaces. Accordingly, present indications are that  $\lambda = 0.90$  to  $1.1$  is a suitable range.

According to a further aspect, the invention provides a method of regenerating a PGM catalyst poisoned by sulphur in the exhaust gas aftertreatment system of a diesel engine, which system does not include a NO<sub>x</sub>-trap, which method comprising modulating  
5 the air/fuel ratio ( $\lambda$ ) of the exhaust gases passing through the catalyst, to  $\lambda = 0.90$ , preferably 0.95, or richer, for a period and under conditions to cause the release of sulphur-containing species from the catalyst or from catalyst components.

Desirably, during the enriched operating condition, catalyst temperatures are in the  
10 range 200° to 500°C, preferably 350° to 500°C, although other temperatures may be used, up to 600°C or more.

In general, increasing the catalyst temperature decreases the time necessary to achieve maximum regeneration, and increasing time at temperature increases the degree of  
15 reactivation. Accordingly, our initial tests have been successful with regeneration times of from 10 seconds to 5 minutes. A suitable time is therefore considered to be from 2 seconds to 10 minutes, preferably in the form of shorter times or pulses, for example 250 milliseconds to 5 seconds.

In a particularly preferred embodiment, the exhaust gas aftertreatment system includes an oxidation catalyst and a downstream particulate or soot filter i.e. it includes our CRT<sup>TM</sup> system as described in EP 0341832. According to this aspect, the invention provides an engine according to the invention wherein the catalyst is an oxidation catalyst and the exhaust gas aftertreatment system also includes a particle or soot filter downstream  
25 of the catalyst.

Gas flow rate has an effect on the time necessary to complete regeneration, and suitable space velocities for the exhaust gases are in the range 5,000 to 50,000 hour<sup>-1</sup>.

30 Although post combustion injection into the engine cylinder is, at present, the preferred method of operation according to the present invention, the invention encompasses direct injection into the exhaust gases, which may be in or close to the exhaust manifold, or into or close upstream of the catalyst housing.

The invention is further described in specific detail in the Examples following. It will be appreciated that the details of particular applications may be altered without departing from the scope of the invention.

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### EXAMPLE 1

A standard production 1997 model year European passenger car with a five cylinder 2.5 litre displacement direct injection Diesel engine that was calibrated to meet European Stage 2 emission levels was used without modification to the engine or its management systems.

The car's exhaust system was equipped with a single round platinum-based oxidation catalyst located in an underfloor position. The catalyst comprised a cordierite monolith having 400 cells/inch<sup>3</sup>, with an external diameter of 5.66 inch and length 6 inch, carrying a washcoat with a platinum loading of 90g/ft<sup>3</sup>.

The vehicle was tested according to the Stage 3 European procedure, without any idle period. In each case the results given are the average of three independent measurements, and are expressed as grams of pollutant/km, which were derived in the normal way. In all of the tests the NO<sub>x</sub> figures were similar, but the NO<sub>2</sub>/NO ratio depended on the catalyst activity. In this experiment only hydrocarbon and carbon monoxide tail pipe measurements were made.

The exhaust gas directly from the engine contained 0.340 and 1.074 g/km hydrocarbon and carbon monoxide respectively.

With the fresh catalyst the tailpipe hydrocarbon and carbon monoxide figures were 0.102 and 0.195 g/km respectively. However, after 17,600 km road operation with diesel fuel typically containing 350 ppm sulphur the tailpipe emissions had risen to 0.287 and 0.823 g/km for hydrocarbons and carbon monoxide respectively. Changing the fuel to a grade containing 38 ppm sulphur followed by normal driving for 1500 km did not

significantly improve the catalyst performance. The tail-pipe emissions were: 0.247 and 0.808 g/km for hydrocarbon and carbon monoxide respectively.

The catalyst in its stainless steel enclosure was then removed from the car and fitted  
5 to the exhaust system of a four-cylinder engine capable of operating slightly rich. It was coupled to a dynamometer mounted on a bench. The fuel used contained 250 ppm sulphur. The catalyst was exposed to exhaust gas corresponding to  $\lambda = 0.95$  for a total period of 5 minutes at a maximum of 500°C. The average temperature was 450°C. After this treatment the catalyst was refitted to the car and retested in the standard way, with the  
10 following results: 0.119 and 0.257 g/km for hydrocarbon and carbon monoxide respectively.

These experiments show the oxidation performance of a catalyst deactivated through use with sulphur containing fuel, can be reactivated by a short reductive process,  
15 even in the presence of sulphur.

### EXAMPLE 2

A similar platinum-based catalyst to that in Example 1, that had been road aged  
20 (with fuel containing typically 350 ppm sulphur) for 18240 km on the same car as in Example 1, gave the following tail pipe emissions in a European Stage 3 test: 0.270 and 0.856 g/km for hydrocarbon and carbon monoxide respectively.

A core (25 mm diameter, 38 mm long) from the middle of this catalyst was taken  
25 with the aid of a diamond tipped tool. The sample was placed into a laboratory test unit. A gas flow containing 400 ppm carbon monoxide, 300 ppm nitric oxide, 100 ppm propene, 12% oxygen, 4.5% water, 4.5% carbon dioxide, and 20 ppm sulphur dioxide with nitrogen balance was established through the catalyst core at a rate corresponding to a space velocity of  $60 \times 10^3 \text{ hour}^{-1}$ . The conversion of nitric oxide to nitrogen dioxide over the  
30 catalyst was 19% at 300°C.

The catalyst core was then subjected to a reductive regeneration procedure at  $\lambda=0.95$ , with the same space velocity as before. The  $\lambda = 0.95$  condition was obtained by

increasing the proportion of carbon monoxide and propene, and decreasing the flow of oxygen. The temperature was gradually increased to 450°C over 15 minutes, during which time a large amount of sulphur dioxide was liberated from the catalyst that was detected by a mass spectrometer. No hydrogen sulphide was detected by the mass spectrometer, nor was any carbonyl sulphide. It was determined that 0.56 wt% of sulphur absorbed on the catalyst had been liberated. These tests showed that the catalyst activity recovered as sulphur was removed.

The gas composition was then reset to that used initially, and the nitric oxide conversion to nitrogen dioxide measure to be 63% at 300°C, showing the ability of the regeneration procedure to reactivate catalyst for the oxidation of nitric oxide to nitrogen dioxide.

It had not previously been believed that it was possible to regenerate a diesel or similar lean-burn catalyst which had been poisoned. Accordingly, this invention significantly expands the envelope of operation as regards fuelling etc. for such fuel efficient engines.



**CLAIMS**

1. A diesel (compression ignition) engine having combustion management means and an exhaust gas aftertreatment system without a NO<sub>x</sub> trap, which system comprising a  
5 platinum group metal (PGM) catalyst liable to be poisoned by fuel sulphur to cause significant degradation of catalyst performance, which engine is fuelled, at least intermittently, by a diesel fuel containing such levels of sulphur as to cause poisoning of the catalyst, wherein the combustion management means is effective to modulate the air/fuel ratio ( $\lambda$ ) to 0.90, preferably 0.95, or richer for a time which is in aggregate  
10 sufficient to cause release of significant quantities of sulphur-containing species from the catalyst or catalyst components, whereby the catalyst is regenerated.
2. An engine according to claim 1, wherein the catalyst is an oxidation catalyst.
- 15 3. An engine according to claim 2, incorporating "common rail" fuel injection, programmed to provide in at least one cylinder, such a quantity of fuel post combustion in the main power stroke, so as to reach, in the exhaust gases,  $\lambda$  of 0.90 or richer.
4. An engine according to claim 1, 2 or 3, wherein the catalyst is an oxidation catalyst  
20 and the exhaust gas aftertreatment system also includes a particle or soot filter downstream of the catalyst.
5. A method of regenerating a PGM catalyst poisoned by sulphur in the exhaust gas aftertreatment system of a diesel engine, which system does not include a NO<sub>x</sub> trap, which  
25 method comprising modulating the air/fuel ration ( $\lambda$ ) of the exhaust gases passing through the catalyst, to  $\lambda = 0.90$ , preferably 0.95, or richer, for a period and under conditions to cause the release of sulphur-containing species from the catalyst or from catalyst components.
- 30 6. Method according to claim 5, wherein  $\lambda$  in the exhaust gases is in the range 0.95 to 1.1 during regeneration.

7. Method according to claim 5 or 6, wherein the catalyst is in the temperature range 200-500°C, preferably 350-500°C, during regeneration.
8. Method according to claim 5, 6 or 7, wherein regeneration is carried out for  
5 20 seconds to 10 minutes.
9. Method according to claim 8, wherein regeneration is carried out using pulses of air/fuel ratio modulation of from 250 milliseconds to 5 seconds in duration.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 00/03379

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 B01D53/94 F02M45/02 F01N3/20

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 B01D F02M F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)  
EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 911 499 A (TOYOTA MOTOR CO LTD) 28 April 1999 (1999-04-28) column 1, line 12 - line 23 column 3, line 49 -column 4, line 13 column 3, line 44 -column 5, line 16 column 5, line 24 - line 36 column 5, line 44 -column 6, line 18 column 6, line 49 -column 7, line 9 column 7, line 39 -column 8, line 42; claims 1-30; figure 1	1-9
A	EP 0 761 286 A (TOYOTA MOTOR CO LTD) 12 March 1997 (1997-03-12) column 1, line 15 - line 47 column 8, line 2 - line 28 column 11, line 22 -column 14, line 36 column 18, line 47 -column 19, line 7; claims 1-12; figures 1-3,9 --- -/-	1-9

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Name and mailing address of the ISA  
European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

Cubas Alcaraz, J

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## C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 858 837 A (SIEMENS AG) 19 August 1998 (1998-08-19) column 2, line 7 -column 3, line 37; claims 1-9; figure 1 -----	1-9

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Information on patent family members

International Application No

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